TestAmerica, Inc.

Dayton Division

Standard Operating Procedure

Analyte or Suite: __Organochlorine Pesticides and PCBs__

Methodology: __Gas Chromatography/Electron Capture Detection__

Reference: __SW-846 Method 8080A; September 1994__

Revision: __5__   Date revised: __May 5, 1999__

File Name: __/usr3/sops/1999/SW-8080A__

Approvals:

_____   _____
Division Manager   Quality Assurance
                                       Coordinator

This is a controlled document and is intended only for internal
use. Unauthorized reproduction of this document is prohibited.

Table of Contents

1. INTRODUCTION AND SCOPE

This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs) in groundwater, solid waste and soils. Table 1 lists the compounds that may be determined by this method and the reporting limit (RL) for each compound.

Table 1. Reporting Limits of Analytes Amenable by 8080

Analyte	Aqueous RL (ug/L)	Soil RL (mg/Kg)
Aldrin	0.20	0.5
alpha-BHC	0.20	0.5
beta-BHC	0.20	0.5
delta-BHC	0.20	0.5
gamma-BHC (Lindane)	0.20	0.5
+ Chlordane, Technical	0.20	0.5
4,4'-DDD	0.20	0.5
4,4'-DDE	0.20	0.5
4,4'-DDT	0.20	0.5
Dieldrin	0.20	0.5
Endosulfan I	0.20	0.5
Endosulfan II	0.20	0.5
Endosulfan sulfate	0.20	0.5
Endrin	0.20	0.5
Endrin aldehyde	0.20	0.5
Heptachlor	0.20	0.5
Heptachlor epoxide	0.20	0.5
4,4'-Methoxychlor	0.20	0.5
+ Toxaphene	0.50	0.5
+ PCB-1016	0.20	0.5
+ PCB-1221	0.20	0.5
+ PCB-1232	0.20	0.5
+ PCB-1242	0.20	0.5
+ PCB-1248	0.20	0.5
+ PCB-1254	0.20	0.5
+ PCB-1260	0.20	0.5
+ designates multicomponent analytes		

1.1. Definitions

Aroclor - Aroclor is the trade name for mixtures containing polychlorinated biphenyls (PCBs). Since each Aroclor is a mixture, they may be described as multicomponent analytes. Aroclors may contain compounds in addition to PCBs but the terms PCBs and Aroclor are commonly used interchangeably. The names of Aroclor mixtures such as 1242 and 1260 refer to the 12 member biphenyl ring and the percent chlorination by weight. Aroclor 1260 is a mixture of isomers composed of 12 member (carbon)

biphenyl rings with 60% chlorination by weight. Aroclor 1016 is an exception and was not named based upon the size of the ring or the percent chlorination. Chromatograms of Aroclors will contain many peaks.

Multi-component Analyte and Single component Analyte - Throughout this SOP, the terms "single component analyte" and "multi-component analyte" are used. Some analytes are mixtures of many compounds of similar structure. These analytes are referred to as multicomponent analytes. A chromatogram of a multicomponent analyte will contain many peaks. Multicomponent analytes include PCBs, toxaphene, and technical chlordane. All other compounds in Table 1 are single component pesticides. Single component analytes contain only one compound. The chromatogram of a single component analyte will contain only one peak.

Primary and Secondary Column - The primary column refers to the column which is normally used for quantitation. The secondary column is normally used for qualification only. Either column can be used for quantitation and reporting if it meets the acceptance criteria.

Extraction Batch - A set of up to 20 samples extracted by the same analyst(s) using the same techniques. Blanks, MSs, LCSs,and MVSs are not included in the 20 count. All other QC samples, including those originating from clients and those originating from TestAmerica (MDLs, PEs), must be included in the 20 count. An extraction batch can be added to until the sample count is 20 and may consist of several extraction sets.

Extraction Set - A set of up to 20 samples extracted by the same analyst(s) using the same techniques on the same day. An extraction set must meet all the criteria of an extraction batch, and the samples and QCIs must all be extracted together on the same day. An extraction set must include at a minimum a blank and LCS and (depending upon sample volume and batch sample count) an MS/MSD.

2. SUMMARY OF METHOD

This method provides gas chromatographic procedures for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used (examples include SOPs for pesticide/PCB extraction by separatory funnel and continuous extraction). An aliquot of the sample extract is injected into a GC equipped with dual columns and dual electron capture detectors. The aliquot is automatically split so that it passes through both columns and both detectors. This allows quantitation and confirmation to take place simultaneously.

3. SAFETY

Employees should comply with all safety policies as presented in the TestAmerica safety manual. Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean up procedures prior to the use of any chemical. This information can be obtained by reviewing the applicable material safety data sheet (MSDS). The bottle labels also provide important information that must be noted. If you have any questions consult your supervisor or safety officer.

Personnel performing this procedure may be working with flammables, poisons, toxins, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn. In addition to other measures prescribed by the division, solvents must be handled in ventilated hoods. It should be noted that samples must be handled with as much (or more) care as any of the materials used in this method due to the unknown nature of their composition. Also, the equipment utilized by this method may contain areas of high temperature and/or high voltage.

The electron capture detectors employed in this method contain radioactive Ni^{63}. Each detector must have a wipe test performed every six months. In accordance with the federally mandated, state administered programs, the wipes are checked for degradation of the radionuclide foil by a certified nuclear counting firm.

4. REAGENTS AND MATERIALS

The following apparatus and materials, or their equivalent, are required. Reagents and materials are considered equivalent if with their use, the analytical and QA/QC requirements in this SOP can be met.

4.1. Apparatus

4.1.1. Gas Chromatograph. Analytical system complete with gas chromatograph suitable for splitless or on-column injections. The system should be equipped with two electron capture detectors and should be capable of splitting the sample into two columns. The Hewlett-Packard Model 5890 or 6890 is preferred.

The data acquisition system must be capable of time stamping all data produced with the correct date and time. If calibration curves are to be used in place of average response factor calibration, the system must be capable of plotting the curves and calculating correlation coefficients.

4.1.2. GC Columns.

4.1.2.1. Column 1: J & W DB-35MS capillary column, 30m x 0.25mm ID x 0.32mm.

4.1.2.2. Col. 2: J & W DB-5MS capillary column, 30m x 0.25mm ID. x 0.32mm.

4.2. Reagents

All reagents must be properly labeled with the reagent identification and concentration, date prepared, expiration date, initials of analyst, and applicable safety information. Labels are available through the centralized purchasing system. The label has a place for the NFPA diamond, which will be used to indicate health (blue), flammability (red), reactivity (yellow), and contact/special (white) information obtained from applicable Material Safety Data Sheets (MSDS) supplied by the vendor.

4.2.1. Hexane (pesticide quality or equivalent) for sample dilutions.

Caution: Hexane is extremely flammable. Keep it away from heat, sparks, and flames. Causes irritation. Toxic by ingestion, inhalation, and absorption. May contain benzene, which is a carcinogen. Gloves, lab coats, and safety glasses must be worn to avoid contact. Avoid inhalation by working with hexane in a fume hood.

NFPA diamond: health = 4, flammability = 3, reactivity = 0, contact = 2.

4.2.2. Isooctane (pesticide quality or equivalent).

Caution: Isooctane is extremely flammable. Keep it away from heat, sparks, and flames. May be toxic by ingestion, inhalation, and absorption. Gloves, lab coats, and safety glasses must be worn to avoid contact. Avoid inhalation by working with isooctane in a fume hood.

NFPA diamond: health = U, flammability = 3, reactivity = 0.

4.2.3. Reagent water Reagent water is water in which an interference is not observed at the method detection limit of the compounds of interest. Reagent Water is prepared by passing water through a carbon filter bed.

4.2.4. Toulene (pesticide quality or equivalent).

Caution: Toluene is extremely flammable. Keep it away from heat, sparks, and flames. May be toxic by ingestion, inhalation, and absorption. Gloves, lab coats, and safety glasses must be worn to avoid contact. Avoid inhalation by working with isooctane in a fume hood.

NFPA diamond: health = 3, flammability = 3, reactivity = 0.

4.3. Standards and Standard Reagents

Caution: The standards used in this SOP may contain one or more known or suspected carcinogens.   Read   all   precautionary information supplied with the standards.   The standards may be extremely flammable, keep them away from heat, sparks, or flame. Gloves and safety glasses should be worn to avoid contact with eyes, and skin.   Any use of these standards in a `manner that causes the release of vapors into the laboratory atmosphere should be conducted within a fume hood.   Hoods are classified as designated areas when working with carcinogens.

4.3.1. Purchasing Standards. The sources of the calibration and verification standards are listed in Table 2.

Table 2. Standard Sources

Analyte	Calibration Standards		Verification Standards	
	Vendor/ Catalog #	Conc. (ug/mL)	Vendor/ Catalog #	Conc. (ug/mL)
Aldrin	R-32291	200 H	U-PPM-808C	1000 HT
alpha-BHC	R-32291	200 H	U-PPM-808C	1000 HT
gamma-BHC (Lindane)	R-32291	200 H	U-PPM-808C	1000 HT
4,4'-DDT	R-32291	200 H	U-PPM-808C	1000 HT
Dieldrin	R-32291	200 H	U-PPM-808C	1000 HT
Endosulfan I	R-32291	200 H	U-PPM-808C	1000 HT
Endrin	R-32291	200 H	U-PPM-808C	1000 HT
Heptachlor	R-32291	200 H	U-PPM-808C	1000 HT
Methoxychlor	R-32291	200 H	U-PPM-808C	1000 HT
beta-BHC	R-32291	200 H	U-PPM-808C	1000 HT
delta-BHC	R-32291	200 H	U-PPM-808C	1000 HT
4,4'-DDD	R-32291	200 H	U-PPM-808C	1000 HT
4,4'-DDE	R-32291	200 H	U-PPM-808C	1000 HT
Endosulfan II	R-32291	200 H	U-PPM-808C	1000 HT
Endosulfan sulfate	R-32291	200 H	U-PPM-808C	1000 HT
Endrin aldehyde	R-32291	200 H	U-PPM-808C	1000 HT
Heptachlor epoxide	R-32291	200 H	U-PPM-808C	1000 HT
Alpha Chlordane	R-32291	200 H	U-PPM-808C	1000 HT
Gamma Chlordane	R-32291	200 H	U-PPM-808C	1000 HT
Chlordane (tech)	R-32021	1000 H	S-4-8065	1000 I
Toxaphene	R-32005	1000 H	S-4-8103	1000 I
*Decachlorobiphenyl	R-32000	200 AC	S-4-8460	200 I
*Tetrachloro-m-xylene	R-32000	200 AC	S-4-8460	200 I
PCB-1016	R-32006	1000 H	A-90123	1000 HT
PCB-1221	R-32007	1000 H	A-90124	1000 HT
PCB-1232	R-32008	1000 H	A-90125	1000 HT
PCB-1242	R-32009	1000 H	A-90126	1000 HT
PCB-1248	R-32010	1000 H	A-90127	1000 HT
PCB-1254	R-32011	1000 H	A-90128	1000 HT
PCB-1260	R-32012	1000 H	A-90129	1000 HT
4,4'-DDT/Endrin	Supelco	200 M	Not applicable	

* Surrogates   S=Supelco, R=Restek, A=Absolute, U=Ultra

H=Hexane, AC=Acetone, HT=Hexane/Toluene Mix, I=Iso-Octane, M=MeOH

4.3.2. Standard storage. Stock standards (mother solutions) can be kept for six months. If the laboratory demonstrates that no degradation has occurred by comparison to the ICVS, the stock

standard may be kept for up to one year. All other standard or spike solutions can be kept for up to six months. Replace standards sooner if it is suspected that the standard has degraded or concentrated. All standards should be stored in teflon capped amber vials at 4°C when not in use. Standards and spikes must be stored separately from any type of sample or sample extract.

4.3.3. Standard logbooks. Each standard used must be completely traceable back to the manufacturer's lot number. Record the date opened, catalog number or description, lot number, and concentration of all standards in the appropriate Standards Logbook. When preparing standard dilutions record the date prepared, reference number (from the Standards Logbook), all information pertinent to the dilution and the initials of the analyst preparing the standard.

4.3.4. Labeling standards. Label each solution vial with the date prepared, standard name, concentration, the Standards Logbook Number, and the preparer's initials. Include safety information if necessary.

4.3.5. General Formula for Preparing Standards. Manufacturers of standards sometimes will change the concentration and composition of standards. Always read the literature provided with the standard so that the concentration and composition of the standard are known. Prior to creating each standard the analyst should calculate the amount of solution needed to get the desired final concentration. Do not assume that the volumes recorded in the standard logbook for the previous standard are correct. To calculate the volume of the mother solution needed to get to a desired concentration use the equation:

$$V_n = \frac{C_f\ V_f}{C_m} \times \frac{1L}{1000mL}$$

Where:

V_n = The volume of mother solution needed in uL
C_f = The final concentration desired in ug/L
V_f = The final volume desired in uL
C_m = Initial concentration (of mother solution) in ug/mL
$\frac{1L}{1000mL}$ = Conversion factor from mL to L

4.3.6. Calibration Standards. Examples are given, in the following sections, that demonstrate how to make a specific volume of each standard. Larger or smaller volumes can be prepared as needed. See section 4.3.1 for specific instructions on where to obtain the calibration mother solutions.

4.3.6.1.   Surrogate Solution. The surrogate solution containing decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) at 200 ug/ml is purchased from Restek. This solution will be used when making the calibration standards as in Table 3.

4.3.6.2.   Table 3 demonstrates the amount of the purchased solutions and SURR needed to prepare 100 mls of the calibration standards.   Dilute all the standards up to final volume with Hexane/Toluene (1:1) in a 100 ml volumetric flask.   Table   4 presents the standard concentrations for single component pesticides.

Table 3. Preparing Single Component Pesticide Calibration Standards

Calib. Standard	Surrogates Level (ug/L)	uL Cal. Stock in 100ml	uL of SURR in 100ml
CAL 1	10	10	5
CAL 2	20	20	10
CAL 3	50	50	25
CAL 4	80	80	40
CAL 5	100	100	50
CAL 6	200	200	100

Table 4. Cal Levels for Single Component Pesticides

Analyte	CAL1 ug/L	CAL2 ug/L	CAL3 ug/L	CAL4 ug/L	CAL5 ug/L	CAL6 ug/L
Adrin	20	40	100	160	200	400
BHC	20	40	100	160	200	400
gamma-BHC	20	40	100	160	200	400
4,4'-DDT	20	40	100	160	200	400
Dieldrin	20	40	100	160	200	400
Encosulfan I	20	40	100	160	200	400
Endrin	20	40	100	160	200	400
Heptachlor	20	40	100	160	200	400
beta - BHC	20	40	100	160	200	400
delta - BHC	20	40	100	160	200	400
4,4'- DDD	20	40	100	160	200	400
4,4' - DDE	20	40	100	160	200	400
Endosulfan II	20	40	100	160	200	400
Endosulfan Sulfate	20	40	100	160	200	400
Endrin Aldehyde	20	40	100	160	200	400
Heptachlor Epoxide	20	40	100	160	200	400
Methoxychlor	20	40	100	160	200	400
Alpha Chlordane	20	40	100	160	200	400
Gamma Chlordane	20	40	100	160	200	400

4.3.6.4.   Toxaphene   calibration   standard.   Prepare
Toxaphene   calibration standards at the   concentrations
defined in Table 5.   Table 5 demonstrates the amount of
1000 ug/ml Restek Toxaphene solution and 200 ug/ml
surrogate needed to prepare 10.0 ml of the calibration
standards.   Dilute   all standards up to final volume
with Hexane in a 10 ml volumetric flask.

Table 5.   Preparing Toxaphene Calibration Standards

Toxaphene Calib. Standard Level	Surrogate Level	ul of 200 ug/ml SURR per 50 ml	ul of 1000 ug/ml Toxaphene per 50 ml
100 ug/L	10 ug/L	2.5 ul	5 ul
200 ug/L	20 ug/L	5.0 ul	10 ul
300 ug/L	30 ug/L	7.5 ul	15 ul
400 ug/L	80 ug/L	20 ul	20 ul
500 ug/L	200 ug/L	50 ul	25 ul

4.3.6.5. Chlordane (technical) calibration standards. Prepare technical chlordane calibration standards at the concentrations defined in Table 6. Table 6 demonstrates the amount of 1000 ug/mL Supelco Standard solution and 200 ug/mL surrogate needed to make 10.0 mL of the calibration standard. Dilute all standards up to final volume with Hexane in a 10 mL volumetric flask.

Table 6. Preparing Chlordane (tech) Calib. Standards

Chlordane Calib. Standard Level	Surrogate Level	uL of 200 ug/mL SURR per 50 mL	uL of 1000 ug/mL Chlordane per 50 mL
100 ug/L	10 ug/L	2.5 uL	5 uL
200 ug/L	20 ug/L	5.0 uL	10 uL
300 ug/L	30 ug/L	7.5 uL	15 uL
400 ug/L	80 ug/L	20 uL	20 uL
500 ug/L	200 ug/L	50 uL	25 uL

4.3.6.6. PCB calibration standards. Prepare PCB calibration standards at the concentrations defined in Table 7. When preparing the calibration standards combine PCB 1242 with PCB 1260. Table 7 demonstrates the amount of 1000 ug/ml Supelco PCB Standard solution and 200 ug/mL surrogate solution needed to prepare 100 mL of each of the calibration standards. Dilute all standards up to final volume in Hexane in a 100 mL volumetric flask. Five point calibrations are performed for PCBs 1242 and 1260. If any of the other PCBs are detected, a five point calibration for that Aroclor must be performed.

Table 7. Preparing PCB Calibration Standards

PCB Calib. Standard Level	Surrogate Level	ul of 200 ug/ml SURR per 100 ml	ul of 1000 ug/ml PCB per 100 ml
12.5 ug/L	2.5 ug/L	*1	*1
25 ug/L	5.0 ug/L	*2	*2
50 ug/L	10 ug/L	5.0 ul	5.0 ul
125 ug/L	15 ug/L	7.5 ul	10 ul
250 ug/L	20 ug/L	10 ul	25 ul
375 ug/L	25 ug/L	12.5 ul	37.5 ul
500 ug/L	30 ug/L	15 ul	50 ul

*1 1/4 dilution of 50 ug/L Standard
* 1/2 dilution of 25 ug/L Standard

4.3.7.   Initial Calibration Verification Standards (ICVS). In the following sections examples that demonstrate how to make a specific volume of each standard are given. Larger or smaller volumes can be prepared as needed. The ICVSs must be prepared from a different source of standards than those used to prepare the calibration standards. See section 4.3.1 for recommended sources for the ICVS mother solutions.

4.3.7.1. Single Component Pesticide ICVS. An ICVS containing the single component pesticides listed in Table 1 is required when running a calibration. A Supelco single component pesticide ICVS standard is available as indicated in Table 2. Prepare 100 mL of the single component pesticide ICV by diluting 2.50 ul of

the Supelco standard and 25.0 uL of the 200 ug/mL surrogate up to 100 mL final volume in Hexane. The concentration of this ICV and surrogates will be 50 ug/L.

4.3.7.2. Toxaphene ICVS. Prepare the toxaphene ICVS at 300 ug/L. Prepare 10 mL of the Toxaphene ICVS by diluting 3.0 uL of the 1000 ug/mL Accustandard solution listed in Table 2 and 2.5 ul of the 200 ug/mL surrogate up to 10.0 mL final volume in Hexane. The concentration of the surrogates will be 50 ug/L.

4.3.7.3. Chlordane ICVS. Prepare the Chlordane ICVS at 300 ug/L. Prepare 10 ml of the Chlordane ICVS by diluting 3.0 ul of the 1000 ug/ml Accustandard solution listed in Table 2 and 2.5 uL of the 200 ug/mL surrogate up to 10.0 ml final volume in Hexane. The concentration of the surrogates will be 50 ug/L.

4.3.7.4. PCB ICVSs. Prepare the PCB ICVSs at 250 ug/L. Any PCBs combined in the calibration standards may also be combined in the corresponding ICVS. Prepare 100 ml of a PCB ICVS dilute 25.0 uL of the 1000 ug/mL Supelco standard and 10 uL of the 200 ug/mL surrogate up to 100 mL final volume in Hexane. The concentration of the surrogates will be 20 ug/L.

5. INTERFERENCES

The sensitivity of this method frequently depends on the level of interferences rather than on instrumental limitations. If interferences prevent identification or detection of the analytes, the sample may need to undergo cleanup procedures. Alumina Column cleanup and Florisil Column cleanup, possibly followed by Sulfur cleanup, may eliminate interferences in the analysis. Gel Permeation Chromatography (GPC) is useful in cleaning extracts which contain high concentrations of hydrocarbons.

Interferences by phthalate esters can pose a major problem when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Otherwise exhaustive clean up of reagents and glassware may be necessary to correct background phthalate contamination.

6. PROCEDURE

6.1. Instrument Preparations

6.1.1. Recommended GC Operating Conditions.

Injection Volume:	1 uL
ECD Temperature:	325 °C
Injection Port Temperature:	200 °C
Initial Temperature:	100 °C
Initial Time:	1 minutes
Rate 1:	25 °C/minute
Final Temperature 1:	150 °C
Final Time 1:	0 minutes-
Rate 2:	10.0°C/minute
Final Temperature 2:	290 °C
Final Time 2:	2.0 minutes
Linear Velocity:	25 cm/second at 290.°C
Split Vent Flow:	50-60 mL/minute
Septum Purge Flow:	0.5 - 1 mL/minute
Make Up Flow:	40-50 mL/minute

6.1.2. Injection Port Maintenance. Due to the low concentrations injected in this method every attempt must be made to ensure that the analyte path in the GC is free from sites of adsorption or activity. Perform injection port maintenance.

6.1.3. Injection Logbook. All injections must be entered into the injection logbook. The logbook must indicate the appropriate sample, standard, or Quality Control Indicator (QCI) designation, the instrument, and the date that the run was started. In the comments section of the injection logbook it may be advantageous to include additional information such as sample weights, sample volumes, final volumes, detailed column information, injection volumes and so forth.

6.1.4. Chromatogram Format. Each chromatogram must be identified with the appropriate sample, standard, or QCI designation, the instrument ID, and the date and time of injection. In addition, the type of column and the injection volume must be documented and traceable through the chromatographic report. The peaks on the chromatogram should be labeled according to retention time. The area of each peak and the corresponding retention time should be summarized in a chart or table. The file ID should be listed on the chromatogram.

6.1.5. The holding time prior to extraction is 7 days for aqueous samples and 14 days for non-aqueous. The holding time after extraction is 40 days. Extracts should be stored at 4 degrees Celcius +/- 2. Extracts are strored separately from standards.

6.2. Daily Analytical Sequence

The following is the order in which a pesticide/PCB analytical sequence is conducted.

6.2.1. Check endrin and DDT breakdown

6.2.2. Pesticide single component standard CCV

6.2.3. PCB 1242/1260 @ 500ug/L

6.2.4. Multicomponent pesticides & PCBs, as necessary

6.2.5. Preparation Blank, as necessary

6.2.6. LCS, as necessary

6.2.7. MS/MSD, as necessary

6.2.8. Analyze samples (maximum of 10 samples or 14 injections)

6.2.9. Repeat steps 1-8

6.3. Chromatographic Library

To create a chromatographic library analyze a mid-range standard of each target analyte under the same conditions that will be used to analyze samples. Single component analytes may be run together as long as all peaks can be separated and identified correctly. Multicomponent analytes cannot be mixed except that PCB 1242 may be mixed with 1260, and PCB 1221 may be mixed with 1254.

6.4. Retention Time Study

Inject three mid-range standards for the analyte over at least a 72 hour period. Standards injected at insufficient time intervals will result in erroneously narrow retention time windows and cause subsequent CCVSs to fall out of control. For each analyte record the three absolute retention times that were obtained from the three standard injections. Calculate the standard deviation across the three absolute retention times. Retention time studies must be repeated periodically as indicated by section 7.1.2.

6.5. Retention Time Windows

The suggested daily retention time window for each single component analyte is equal to the absolute retention time of the analyte in the first CCVS of the day +/- 3 times the standard deviation determined in section 6.4. If the samples or QCIs are being run directly after a curve, the daily retention time window for each single component analyte is equal to the absolute

retention time of the analyte in the midpoint standard of the curve +/- 3 times the standard deviation determined in section 6.4. In those cases where the standard deviation for a particular analyte happens to be zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window. Note that this is a suggested window size. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

6.6. Method Detection Limit (MDL) Study

Method detection limit studies are required to be performed annually per the MDL SOP.

6.7. Method Validation Sample (MVS) Analysis

6.7.1. This method must be validated by demonstrating that the precision and accuracy limits in Table 8 can be met.

Table 8. MS, LCS, MVS Acceptance Criteria

Analyte	Spike Amount*	s limit (ug/L)	x range (ug/L)	p range (%)
Aldrin	1.0	0.42	0.54-1.12	42-122
alpha-BHC	1.0	0.48	0.49-1.22	37-134
beta-BHC	1.0	0.64	0.39-1.30	17-147
delta-BHC	1.0	0.72	0.50-1.18	19-140
gamma-BHC (Lindane)	1.0	0.46	0.43-1.16	32-127
Chlordane	50	10	27-54.3	45-119
4,4'-DDD	1.0	2.8	0.48-1.26	31-141
4,4'-DDE	1.0	0.55	0.54-1.30	30-145
4,4'-DDT	1.0	3.6	0.46-1.37	25-160
Dieldrin	1.0	0.76	0.58-1.24	36-146
Endosulfan I	1.0	0.49	0.57-1.41	45-153
Endosulfan II	1.0	6.1	0.22-1.71	D-202
Endosulfan Sulfate	1.0	2.7	0.38-1.32	26-144
Endrin	1.0	3.7	0.51-1.26	30-147
Heptachlor	1.0	0.40	0.43-1.00	34-111
Heptachlor epoxide	1.0	0.41	0.56-1.32	37-142
Toxaphene	50	12.7	278-55.6	41-126
PCB-1016	50	10	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	8.4	12.2	4.17-11.7	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	8.4	10.4	3.14-9.20	8-127

* This is the concentration of analyte (in ug/L).
s= standard deviation in ug/L (not % RSD)
x= mean concentration range limit for four LCSs as MVSs
p= percent recovery limit range for matrix spike and LCS

6.7.2. Method validation samples will be provided by extraction personnel. They must be extracted in the same batch and analyzed in the same batch. MVSs must be analyzed before bringing this method on line. MVS analysis must be repeated periodically as specified in section 7.3.2.

6.7.3. The compounds contained in the MVSs will depend upon the type of analytes being targeted: single component or multicomponent. Analyze four Laboratory Control Samples (LCSs) which have been spiked with each single component analyte at the levels listed in Table 8. Each target analyte (including multi-component analytes) requires a valid method validation study.

6.7.4. Calculate the mean concentration (x) and the standard deviation (s) for each analyte. To validate the method, the s and x limits in Table 8 must be met. The standard deviation and mean concentration limits in Table 8 are based on the concentration of the analytes in 1.0L of water. If the s and x criteria cannot be met, corrective action must be performed as in section 7.3.4.

6.7.5. The following equations are used to calculate the concentration of an analyte in an MVS, matrix spike, or LCS.

$$\text{Spike Concentration (ug/L)} = \frac{M_a}{V_i}$$

where:

M_a = The mass of analyte (in ug) spiked into the sample or QCI.
V_i = Initial Volume of Sample or QCI (volume extracted) in L.

6.8. Initial Calibration Curve

The initial calibration curve consists of a minimum of five standards analyzed at different concentrations. The lowest standard should be at a concentration near but above the MDL and the other concentrations should define the working range of the detector. There are three techniques which can be used to evaluate calibration curves per this SOP: average response factor, linear fit, and quadratic fit calibration. In all cases the calibration curve is used to quantitate samples and QCIs. An initial calibration curve for each target analyte must be analyzed and evaluated before any hit for that analyte can be quantitated. Initial calibration curves must be validated daily with a CCVS.

6.8.1. Single Component Pesticide Initial Calibration. Initial calibration curves for each single component pesticide must be validated on both columns before bringing this method on line. Single component pesticide calibration curves must be reanalyzed when indicated by section 7.5.2.

6.8.2. Toxaphene Initial Calibration. Initial calibration for toxaphene must be performed when indicated by section 7.5. To perform toxaphene initial calibration analyze at least five standards at the concentrations listed in Table 5.

6.8.3. Technical Chlordane Initial Calibration. Initial calibration for technical chlordane must be performed when indicated by section 7.5. To perform initial calibration for chlordane, analyze at least five standards at the concentrations listed in Table 6.

6.8.4. PCB Initial Calibration. Initial calibration for PCBs 1242 and 1260 must be performed on the primary column before bringing this method on line. Additional curves and updating of curves must be performed when indicated by section 7.5. To perform initial calibration for an PCB, analyze at least five standards at the concentrations listed in Table 7. PCB 1242 may be combined with PCB 1260. Additional Aroclors should be calibrated for when detected.

6.8.5. Understanding the proper use of calibration curves is essential to the success of this method. Always use the average response factor calibration whenever possible. If it is necessary to use a calibration curve, the curve must be plotted on paper in order to decide if a calibration curve is appropriate.

6.8.6. Average Calibration Factor For each of the standards, calculate the calibration factor of each compound using the equation:

$$\text{Calibration Factor (CF)} = \frac{\text{Total Area of Peak(s)}}{\text{Mass Injected (nanograms)}}$$

Calculate the average of the calibration factors and the standard deviation. Use the CF and the standard deviation to calculate the percent relative standard deviation (%RSD). When the calibration factors of the standards demonstrate less than 20 %RSD for all target analytes, linearity through the origin can be assumed. This criteria (RSD<20%) must be achieved if the average calibration factor is to be used for quantitation.

6.8.7. Linear Fit Calibration. In order to use linear fit calibration, the integrator or data system must be capable of plotting and evaluating a calibration curve by calculating the correlation coefficient against the first order equation listed in Section 6.13.3.2. The criteria for using this equation is that the correlation coefficient must be greater than or equal to 0.980. If the correlation coefficient is less than 0.980, the linear fit calibration cannot be used for calibration.

6.8.8. Quadratic Fit Calibration. In order to use quadratic fit calibration, the integrator or data system must be capable of plotting and evaluating a calibration curve by calculating the

correlation coefficient against the second order equation listed in Section 6.13.3.3. If a quadratic fit is to be used for calibration, the correlation coefficient must be greater than or equal to 0.995.

6.9. Initial Calibration Verification Standard (ICVS)

See Section 4.3.7 for directions on preparing the ICVSs. ICVS analysis is required immediately following each curve. The ICVS should be quantitated against the initial calibration curve. See Sections 7.6.3 - 7.6.4 for the criteria and corrective action for ICVSs.

6.10. DDT and Endrin Breakdown

DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'- DDE and 4,4' - DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in Method 8000. Calculate percent breakdown as follows:

$$\text{\% breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE+DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\text{\% breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

If either alone exceeds 20% perform GC system maintenance and begin a new calibration sequence.

This check must be performed both on the initial calibration and on each subsequent day of continuing calibration. It must pass the above criteria for analysis to proceed.

6.11. Continuing Calibration Verification Standard (CCVS)

The CCVSs used in this SOP are simply the midrange standards that were prepared in section 4.3.6. The CCVSs must be analyzed to verify that the calibration curves and retention time windows are still valid. The CCVSs are not used for calibration or quantitation. CCVS analysis is necessary when indicated by section 7.7.2.

6.11.1. Single Component Pesticide CCVS. To perform calibration verification for the single component pesticides analyze the mid-range standard prepared as in section 4.3.6.3.

6.11.2. Toxaphene CCVS. To perform calibration verification for toxaphene, analyze the mid-range calibration standard prepared in section 4.3.6.4.

6.11.3. Technical Chlordane CCVS. To perform calibration verification for technical chlordane, analyze the mid-range calibration standard prepared in section 4.3.6.5.

6.11.4. PCB CCVS. To perform calibration verification for a PCB, analyze the midrange calibration standard for that PCB, prepared in section 4.3.6.6. PCB 1242 may be mixed with PCB 1260. Mixing of PCBs for CCVS analysis should only be done if the same PCBs were mixed in the initial calibration curve.

6.11.5. Retention Time Windows. The retention time windows are set according to the first CCVS of the day (or the midpoint standard of the curve if no CCVS is available) as in section 6.5. If any subsequent CCVSs do not meet the retention time window criteria in section 7.1.3 corrective action must be performed as in section 7.1.4.

6.11.6. Evaluating CCVSs. Quantitate all CCVSs against the initial calibration curve. For each compound, calculate the standard recovery using the initial calibration curve. The same calibration (average RF, linear or quadratic) must be used for the standard as for the samples. If the recovery results do not meet the criteria in section 7.7.3 ($\pm$ 15 % of true value), corrective action must be performed as in section 7.7.4.

6.12. Sample and Quality Control Indicator (QCI) Analysis

6.12.1. Preparation Blanks. Analyze the preparation blank before analyzing the samples for an extraction batch. Quantitate all preparation blanks against the initial calibration curve. Preparation blanks must meet all the criteria in section 7.8.3, or corrective action must be performed as in section 7.8.4.

6.12.2. Laboratory Control Samples. The amount of analyte (in ug) which was spiked into the LCS before extraction is listed in Table 8. Equations are given in section 6.7.5 for calculating spike concentration of each analyte in the LCS. Whenever possible analyze the LCS immediately following analysis of the preparation blank for an extraction batch. This SOP only requires evaluation (data review) of LCS data when a matrix spike is out of control. Any LCSs that are evaluated must pass the criteria in section 7.10.3. Quantitate LCSs against the initial calibration curve. If it is discovered that an LCS is out of control, corrective action must be performed as in section 7.10.4.

6.12.3. Matrix Spikes. The concentration of analyte (in ug/L)

which was spiked into the matrix spike before extraction is listed in Table 8. Equations are given in section 6.7.5. for calculating the spike concentration of each analyte in the matrix spike. Whenever possible analyze the matrix spike immediately following analysis of the laboratory control sample for an extraction batch. Quantitate all matrix spikes against the initial calibration curve. If the matrix spike does not meet the criteria in section 7.8.3. performance corrective action as in section 7.8.4.

6.13. Data Interpretation

6.13.1.   Qualitative Versus Quantitative Analysis. Data interpretation consists of two steps, qualitative interpretation and quantitative interpretation. Qualitative interpretation involves identifying the analytes that are present. Analytes are identified according to their retention time on the primary column. All identifications are confirmed using the secondary column, pattern recognition, or relative peak ratios. Quantitative interpretation involves determining the concentrations of the analytes that are present. All analytes are quantitated using the initial calibration curve.

6.13.2.   Qualitative Analysis. The first step in evaluating the data is qualitative analysis. For a single component analyte to be identified both columns must exhibit a peak within the analyte's retention time window. For multicomponent analytes (toxaphene, chlordane, and PCBs) identifications are based mostly on pattern recognition, but retention time windows can be used to supplement this process. Second column confirmation is not required for multicomponent analytes or for samples that do not have hits above the reporting limit.

6.13.2.1.   Pattern Recognition of Multicomponent Analytes. Each multicomponent analyte shows a distinctive chromatographic pattern which is used to identify that compound in a sample. To determine if a multicomponent analyte is present, compare the sample chromatogram to the daily standard or to the chromatographic library. If the multicomponent analyte is present in the sample the relative response of the peaks in the standard chromatogram should be similar to the response of the corresponding peaks in the sample chromatogram. For example, if the first peak in the standard is half the size of the second peak, a similar ratio should be observed in the sample. In addition, most of the major peaks observed in the standard should also appear in the sample. Be aware that degradation can alter the appearance of a sample hit, making it harder to recognize.

6.13.2.2.   Sample interferences. Sample chromatograms often contain peaks not present in the standard chromatogram. This is because samples frequently contain interferences. Interferences could also coelute with analyte peaks in a chromatogram and change the relative peak ratios. The possibility of interferences must be considered before a multicomponent hit is

invalidated because of a poor match to the standard chromatogram.

6.13.2.3.   Special Problems With PCBs. The analyst must carefully scrutinize all chromatograms for 1221 because only a few relatively small peaks identify this PCB. In addition, there are few unique peaks which can be used to differentiate between the PCBs 1016, 1232, 1242, and 1248. Therefore, their identification must be made primarily upon differences in the ratios of the peaks present.

6.13.2.4.   GC/MS confirmation is allowed for analytes which are detectable by GC/MS, about 10ppm or greater in the sample. A standard and blank must also be analyzed with the sample on the GC/MS. A GC/MS operator will compare the standard spectrum with the sample spectrum to confirm the identification. _This is for qualification purposes only. No quantification is done by GCMS.

6.13.3.   Quantitative Analysis. The second step in evaluating data is quantitative analysis. Quantitative analysis only takes place after the qualitative techniques in section 6.13.2 have been used to confirm a hit. For multicomponent analytes (toxaphene, chlordane, and PCBs) a minimum of 3 distinct peaks must be used for quantitative analysis. For best quantitation of multicomponent analytes use all distinct peaks. Quantitation can only occur on a column (primary or secondary column) if all initial calibration and CCVS criteria have been met on that column. QCIs must be quantitated on the primary column whenever possible. It is possible that an interference on the primary column could cause a QCI to be out of control. Therefore, if a QCI does not meet acceptance criteria on the primary column and the secondary column has passed initial calibration and CCVS criteria for that analyte, the QCI may be reevaluated on the secondary column. Sample and QCI quantitation results must be less than the upper limit of the initial calibration curve. Dilution is required if any target analyte exceeds the upper calibration limit. There are three calibration techniques acceptable to use for quantitation: average calibration factor calibration, use of a first order (linear) calibration curve, and use of a second order (quadratic) calibration curve.

6.13.3.1. Average Calibartion Factor. When using average calibrationfactor for calibration, calculate the concentration of the analyte using the following equation:

$$\text{Concentration (ug/L)} = \frac{(A_x)\,(V_f)\,(D_f)}{(CF_a)\,(V_i)}$$

where:

A_x = Area counts for the analyte in the sample.
V_i = Initial Volume of sample (volume extracted) in mL.
V_f = Final Volume of sample extract in mL.
D_f = Dilution Factor. The dilution factor is the inverse of the dilution. Example: for a 1 to 10 dilution (1/10) the dilution factor is equal to 10 (actually 10/1).
CF_a = Average calibration factor from the initial calibration curve in ug/L/area counts.

For soil calculation substitute W (weight of sample extracted) for V_i. Concentration is in ug/Kg.

6.13.3.2. Linear Fit Calibration. When using linear fit calibration the data system or integrator must be capable of automatically calculating the concentration of each sample. Any preparation or dilution multipliers can be factored in afterwards by the analyst or included in the data system's calculation. The following equation is given to help the analyst understand how the numbers are generated.

$$\text{Concentration (ug/L)} = \frac{([m]\,[A_x] + b)\,(V_f)\,(D_f)}{(V_i)}$$

where:

$([m]\,[A_x] + b)$ = Concentration of analyte in sample extract, calculated by data system or integrator (ug/L).
V_i = Initial Volume of sample (volume extracted) in mL.
V_f = Final Volume of sample extract in mL.
D_f = Dilution Factor. The dilution factor is the inverse of the dilution. Example: for a 1 to 10 dilution (1/10) the dilution factor is equal to 10 (actually 10/1).

For soil calculation substitute W (weight of sample extracted) for V_i. Concentration is in ug/Kg.

6.13.3.3. Quadratic Fit Calibration. When using quadratic fit calibration the data system or integrator must be capable of automatically calculating the concentration of each sample. Any preparation or dilution multipliers can be factored in afterwards by

the analyst or included in the data system's calculation. The following equations are given to help the analyst understand how the numbers are generated.

$$\text{Concentration (ug/L)} = \frac{([a][A_x^2] + [b][A_x] + c)(V_f)(D_f)}{(V_i)}$$

where:

$([a][A_x^2] + [b][A_x] + c)$ = Concentration of the sample extract, calculated by data system or integrator (ug/L).

V_i = Initial Volume of sample (volume extracted) in mL.
V_f = Final Volume of sample extract in mL.
D_f = Dilution Factor. The dilution factor is the inverse of the dilution. Example: for a 1 to 10 dilution (1/10) the dilution factor is equal to 10 (actually 10/1).

For soil calculation substitute W (weight of sample extracted) for V_i. Concentration is in ug/Kg.

If a dry weight result is required please see the Dry Weight SOP for assistance.

6.13.3.4. Quantitative Confirmation. It is possible that one column will exhibit interference which adversely effects the quantitation but allows for confirmation of the analyte. For this reason all single component analyte hits must be quantitatively confirmed by comparing the two concentration values obtained off the primary and secondary columns. Calculate the concentration of the analyte on both columns. In the instances where the relative percent difference between the two results exceeds 40 % and there is no evidence of chromatographic anomalies or interferences, then the higher result is reported and the data user is notified of the possible problem.

6.13.3.5. Toxaphene and Chlordane. If it is determined that toxaphene or chlordane is present, a calibration curve for that analyte must be validated (see section 6.8 to 6.11) before quantitative analysis can proceed. Once a calibration curve is in place the sample must be reanalyzed and quantitated using the curve.

6.13.3.6. PCBs. Calibration curves are not normally run or validated for all PCBs. If it is determined that a PCB is present, for which no valid calibration curve exists, a calibration curve for that PCB must be validated (see section 6.8 to 6.11) before quantitative analysis can proceed. Once a calibration curve is in place the sample must be reanalyzed and quantitated using the curve.

6.13.3.7. Multicomponent Quantitative Analysis. To quantitate multicomponent analytes discern at least distinctive peaks in the sample chromatogram that correspond to unobstructed peaks in the standard chromatograms (standards from the curve). Total the area of these peaks in the sample. For each curve standard, total the area of the corresponding peaks. If the average response factor calibration technique is to be used, calculate standard response factors for each

curve standard from the total areas. Then from the standard response factors calculate an average response factor. Alternatively, the total areas from each curve standard can be used to produce a linear or quadratic calibration curve. Finally, the average response factor or the calibration curve is used to calculate sample concentrations.

6.13.3.8. Report results without correction for recovery data when sample spikes are performed. When sample duplicates are analyzed do not average or combine results. If only one multicomponent analyte is present, the first step is to identify the peaks of the pattern which are characteristic of the analyte, and free of interferences. The analyst should identify as many strongly responding peaks due to the presence of the analyte and free from interferences as possible. Frequently, either the primary or confirming column will have less problem with interferences. Use whichever column is easier to work with as long as that column has passed initial calibration and CCVS criteria. Once this is done for the sample, the analyst should identify the same peaks in the standard (on the same column) and calculate a response factor for the analyte based upon only these peaks.

6.13.3.9. Multicomponent Analyte Plus Single Component Analyte. If a single component pesticide is coeluting with a peak of a multicomponent analyte the analyst should check the confirming chromatogram to determine if these peaks coeluted on the secondary column. If the peaks did not coelute on the secondary column and the secondary column passed calibration criteria, calculate the concentrations using the data off of the secondary column. If they coelute on both columns, the concentration of the multicomponent analyte can be calculated as usual provided the coeluting peak is not used. For the single component analyte, the analyst must report the value as determined from the column showing the least interference anf flag the value with a comment indicating it to be only an estimate due to coeluting interference.

6.13.3.10 Multiple Multicomponent Analytes. When two or more multicomponent analytes are present in the same sample the situation is more difficult. To identify more than one analyte both retention times of peaks and pattern recognition must be used. Once the analytes are identified, if three or more peaks can be identified that are characteristic of just one of the analytes, the analyst proceeds as in section 6.13.3.8. If only one or two characteristic peaks are present, the analyst can use those peaks to determine estimated areas for additional peaks as in section 6.13.3.9.

When there are no characteristic peaks free from interferences, use professional judgment and report the identity of the analyte as the standard which matches the pattern best. Flag the data as a "tentative identification" and include a comment or case narrative explaining how the hit was quantitated.

7. QUALITY CONTROL

Each division that uses these methods is required to conform to the quality control program as outlined in the QAP. The laboratory must

maintain records to document the quality of the data generated and these records will be regularly audited. The records must be complete and well organized. Quality control indicators (QCIs) such as preparation blanks, matrix spikes, and laboratory control samples are compared with established acceptance criteria to determine if the results are in control.

The experience of the analyst performing GC analyses is invaluable to the success of this method. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly.

7.1. Retention Time Study

7.1.1. Definition & Use of Retention Time Study

The purpose of a retention time study is to establish acceptable retention time windows to use for qualification and quantitation of target analytes. A retention time study consists of three standards that were injected over at least a 72 hour period. The results of this study will allow the analyst to determine how wide the retention time windows will be. The width of the windows will not change until another retention time study has been performed. However, the position of each window on the chromatogram (the center of each window) will be updated daily using the CCVS. Please see Table 9 For estimated retention times.

7.1.2. Frequency of Retention Time Study

Retention time studies must be performed for each single component analyte and on both columns before bringing this method on line. Retention time studies must be re-done for both columns whenever a new column is installed. Retention time studies do not need to be performed daily. However, the retention time windows must be updated daily using the CCVS.

7.1.3. Criteria for Retention Time Windows

Retention time windows are intended to last over an entire day. The windows are set according to the first CCVS of the day. If any subsequent CCVSs in the analytical sequence have an analyte which does not fall within its determined retention time window, the run is out of control and corrective action must be performed. The retention Time window is ± 3 standard deviations.

7.1.4. Corrective Action for Retention Time Windows

If a run is determined to be out of control according to the criteria in section 7.1.3, all samples and QCIs must be reevaluated. If the system is capable, it is acceptable to update the retention time windows according to the CCVS that was out, and then requantitate all the subsequent data. If the system is not capable of storing and reevaluating data, any samples or QCIs that were run with the invalid retention time windows will have to be rerun after new retention time

windows can be assigned by running a new CCVS.

7.1.5. Documentation for Retention Time Study

The retention time study should be filed in a manner that will ensure that it can be easily retrieved and referenced to the correct instrument.

Table 9. Estimated Retention Times

Analyte	Column DB-35MS minutes	Column DB-5MS minutes
Aldrin	17.17	14.49
alpha-BHC	13.26	10.16
beta-BHC	14.95	10.90
delta-BHC	16.19	11.80
gamma-BHC (Lindane)	14.64	11.13
Chlordane	MP	MP
4,4'-DDD	22.84	18.94
4,4'-DDE	20.99	17.63
4,4'-DDT	23.87	20.13
Dieldrin	21.34	17.71
Endosulfan I	20.32	16.89
Endosulfan II	23.12	18.67
Endosulfan sulfate	24.64	20.01
Endrin	22.50	18.40
Endrin aldehyde	24.11	19.25
Heptachlor	16.00	13.40
Heptachlor epoxide	19.07	15.74
Methoxychlor	26.47	21.92
Toxaphene	MP	MP
PCB-1016	MP	MP
PCB-1221	MP	MP
PCB-1232	MP	MP
PCB-1242	MP	MP
PCB-1248	MP	MP
PCB-1254	MP	MP
PCB-1260	MP	MP
MP designates multi peak analytes		

The Retention Times listed can vary by ± 5 minutes based on column and instrument conditions.

7.2. Method detection Limit (MDL) Studies

Method detection limit studies are required to be performed annually per the MDL SOP.

7.3. Method Validation Sample (MVS)

7.3.1. Definition & Use of MVS

The purpose of the MVS is to verify that the method can generate precise and accurate analytical data. Method validation samples consist of four replicate 1L aliquots of reagent water, spiked, extracted, and analyzed. The solution used to spike MVSs should be from the same source as the calibration standards. The samples must be extracted in the same batch and analyzed in the same batch. They are used to validate new analyst and new instruments, and to validate changes in analytical equipment or techniques. See the appropriate extraction SOP for specific instructions on preparing the MVSs.

7.3.2. Frequency of MVS

If this method is to be used to analyze for single component pesticides in Table 8, the MVS must contain all the single component pesticides, in Table 8, which are targets. If this method is not to be used to analyze for the single component pesticides in Table 8, use the target multicomponent analyte(s) for MVS analysis. A set of method validation samples must be analyzed, at least once, by each analyst performing this method. A set of method validation samples must be analyzed on each instrument and each type of column that will be used to perform this method. However, each analyst does not have to analyze a set of method validation samples on every instrument and every column. Method validation must be repeated whenever a significant change in the method or instrumentation is made which could cause the previous MVS to become invalidated. Examples of significant changes include: changing extraction techniques, converting to an on-column injector, or switching to a new type of column. Insignificant changes include: buying new glassware that is mechanically the same as the old glassware, performing injection port and column maintenance, or installing a new column that is the same type as the old column.

7.3.3. Criteria for MVS

The average amount of analyte recovered (in ug/L) from the four MVSs, must fall within the mean concentration range (x) in Table 8. The standard deviation of the recovered concentration of a target analyte (in ug/L), across the four MVSs, must meet the standard deviation limit (s) in Table 8.

7.3.4. Corrective Action for MVS

If an MVS fails to pass the criteria in section 7.3.3, the MVS may be rerun just for the analyte(s) that failed. However, repeated failure for any analyte indicates a general problem and invalidates the MVS analysis. If a general problem is indicated, it must be identified and corrected, and the MVSs must be reextracted and/or reanalyzed for all analytes.

7.3.5. Documentation for MVS

.One method validation study may serve several purposes including analyst training, method validation, and instrument validation. The MVSs should be filed in a manner that will ensure that they can be easily retrieved for all intended purposes.

7.4. Analyst Certification

This method is restricted to use by, or under the supervision of analysts trained in the use of gas chromatographs and skilled in the interpretation of the chromatograms as a qualitative and quantitative tool (see Analyst Certification SOP).

7.5. Initial Calibration Curve

7.5.1. Definition & Use of Initial Calibration Curve

The purpose of an initial calibration curve is to relate detector response to sample concentration. It also provides a way of verifying that detector response, over a predetermined concentration range, can be predicted using a mathematical equation. If the response were erratic, there would be no accurate way to relate response to concentration and the curve would not pass. The initial calibration curve consists of a minimum of five standards run at the levels defined in section 4.3.6. The lowest standard should be slightly higher than the reporting limit. The other standards should be distributed over the working range of the detector. The highest standard will define the upper limit of the working range. The initial calibration curve will be used to quantitate samples and QCIs.

7.5.2. Frequency of Initial Calibration Curve

Initial calibration curves must be run before bringing this method on line. Sections 7.5.2.1 and 7.5.2.2 define the curves that are required for each type of analysis. Initial calibration curves must be rerun each time the CCVS criteria in section 7.7.3 cannot be met and each time a significant change is made to the instrument which could invalidate the previous initial calibration curve. These are similar to the significant changes outlined for an MVS except that they specifically relate to the instrument. Examples of significant changes for an initial calibration curve include: conversion to on-column injection, increasing the ramp rate to speed up the runs, or changing columns. Due to the high variability among individual columns, it would be inappropriate to assume that every column of the same type is linear over the same range. Therefore, an initial calibration curve is required whenever changing columns even if the new column is of the same type as the old column. Examples of insignificant changes for an initial calibration curve include: adding an extra ramp to bake out the column after all the analytes have eluted, replacing a septum, or performing injection port and column maintenance.

7.5.2.1. Pesticides Initial Calibration Frequency

Initial calibration curves must be maintained for each of the single

component pesticides that are target analytes. In addition, if it is determined that a sample or QCI contains a hit for a multicomponent pesticide, an initial calibration curve must be validated for that pesticide. If an initial calibration curve already exists for the pesticide, a CCVS may be run to see if the curve is still valid. If the CCVS passes all criteria in section 7.7.3, the sample or QCI must be reanalyzed after the CCVS and quantitated using the curve. If no existing initial calibration curve can be validated for the pesticide, a new initial calibration curve must be analyzed. Once a new curve has been analyzed that passes all the criteria in section 7.5.3, the sample or QCI must be reanalyzed and quantitated using the new curve.

7.5.2.2. PCB Initial Calibration Frequency

Initial calibration curves must be maintained for PCBs 1242 and 1260. In addition, if it is determined that a sample or QCI contains a hit for a different PCB, an initial calibration curve must be validated for that PCB. If an initial calibration curve already exists for the PCB, a CCVS may be run to see if the curve is still valid. If the CCVS passes all criteria in section 7.7.3, the sample or QCI musts be reanalyzed after the CCVS and quantitated using the curve. If no existing initial calibration curve can be validated for the PCB, a new initial calibration curve must be analyzed. After a new curve has been analyzed, and it has passed all the criteria in section 7.5.3, the sample or QCI must be reanalyzed and quantitated using the new curve.

7.5.3. Criteria for Initial Calibration Curve

7.5.3.1. Average Calibration Factor

Average calibration factor assumes that the calibration is linear through the origin. To express this line mathematically use the equation:

$$Y = mX$$

Where:
 Y = amount
 X = area response
 m = slope

When the response factors of the standards demonstrate less than 20 % RSD for all target analytes, linearity through the origin can be assumed. This must be achieved if the average response factor is to be used for quantitation.

7.5.3.2. Linear Fit Calibration

Linear fit calibration is similar to average response factor calibration in that they both assume linearity. However, it differs from average response factor calibration in that it doesn't necessarily pass through the origin. To express this sort of a line mathematically use a first order equation:

$$Y = mX + b.$$

> Where:
> Y,m, and X are the same as in Section 7.5.3.1.
> b = constant as determined by data system

The criteria for using this equation is that the correlation coefficient must be greater than or equal to 0.995. If the correlation coefficient is less than 0.995, the linear fit calibration cannot be used for calibration.

7.5.3.3. Quadratic Fit Calibration

Quadratic fit calibration does not assume that the response of the detector is linear over the range of the curve. It uses the second order equation:

$$Y = mX^2 + bX + c$$

> Where:
> Y,m,X, and b are the same as in Sections 7.5.3.1 and
> 7.5.3.2
> c = constant as determined by data system

to relate the responses of the detector to a curved line that travels over the working range. If a quadratic fit is to be used for calibration, the correlation coefficient must be greater than or equal to 0.995.

7.5.4. Corrective Action for Initial Calibration Curve

Since the initial calibration curves are used for calibration, an analyte hit will not be reported if that analyte failed the initial calibration curve criteria on either column. For samples that have no hits for any target analyte, only one column must pass initial calibration curve criteria. If a compound fails the initial calibration curve criteria, reanalyze for the compound that failed. If any target analyte that failed initially fails upon reanalysis a problem is indicated. Perform any corrective actions necessary, and reanalyze the curve for all compounds.

7.5.5. Documentation for Initial Calibration Curve

The %RSD or correlation coefficient of each compound should be summarized in a table or report. The initial calibration curve should be filed in a manner that will ensure that it can be easily retrieved and referenced to all associated samples.

7.6. Initial Calibration Verification Standard (ICVS)

7.6.1. Definition & Use of ICVS

The purpose of the ICVS is to verify that the calibration standards were prepared properly and that they have not degraded significantly since the time they were made. It also serves as a check on the purity of the calibration standards. The ICVS contains all the compounds that are found in the initial calibration curve. It must be obtained from a different source than the one used to obtain the calibration standards.

7.6.2. Frequency of ICVS

ICVS analysis is required after every initial calibration curve. Normally this will involve the single component pesticides and PCBs 1242 & 1260. However, when hits are found for other pesticides or PCBs, they will also require curves and ICVSs.

7.6.3. Criteria for ICVS

Quantitate the ICVS against the initial calibration curve. The quantitated results of the ICVS should be within +/-30% of the true concentration of each analyte in the ICVS.

7.6.4. Corrective Action for ICVS

If the ICV recovery is outside the criteria listed in 7.6.3. it can be re-analyzed. If a successful ICVS cannot be analyzed, the problem must be corrected and a new initial calibration curve must be analyzed for the compounds that are out of control. Analytical results cannot be accepted until an acceptable ICVS has been analyzed.

7.6.5. Documentation for ICVS

Record the percent difference determined in section 7.6.3 on the chromatogram or in a report. The ICVS should be filed in a manner that will ensure that it can be easily retrieved and referenced to the associated calibration curve.

7.7. Continuing Calibration Verification Standard (CCVS)

7.7.1. Definition & Use of CCVS

The purpose of the CCVS is to establish that the response of the ECD has not changed significantly since the initial calibration curve was analyzed. Over time the detector's response to any given concentration will change. As the response of the detector changes, the initial calibration curves must be rerun to ensure that samples and QCIs are quantitated accurately. The CCVS is also used to verify that retention time windows remain accurate over the course of an analytical sequence. The CCVS consists of standard run at the same concentration as the midpoint standard from the curve. The CCVSs required daily for pesticides must contain all the single component pesticides which are target analytes. The CCVS required daily for PCB analysis contains the

PCBs 1242 and 1260. In addition, if it is determined that a sample or QCI contains a target analyte which was not in the CCVS, a CCVS can be analyzed for that compound, assuming an initial calibration curve already exists for the compound. If the CCVS passes, the sample in question must be reanalyzed after the CCVS, and the calibration curve can be used for quantitation. If the CCVS fails, a new initial calibration curve must be analyzed, and then the sample in question must be reanalyzed and quantitated using the new curve. In general terms, CCVSs must pass to confirm that an initial calibration curve is still valid, and that the curve can be used for accurate quantitation.

7.7.2.   Frequency of CCVS

CCVSs are run at the beginning of a daily analytical sequence (unless a new curve is being analyzed), at the end, and after every 10 samples or 14 injections, whichever comes first. Blanks, MSs, LCSs, and MVSs are not included in the 10 count. All other QC samples, including those originating from clients and those originating from TestAmerica (MDLs and PEs), must be included in the 10 count. The 14 injection limit is meant to allow the analyst to run 10 samples plus a blank, an LCS, and two matrix spikes. Since LCSs and matrix spikes are done with every 10 samples, this should give the analyst enough room to keep extraction batches together. It is also meant to prevent any run from lasting an excessive amount of time due to an unusually high number of QCIs. If samples are run after a calibration curve, or if several CCVSs are injected sequentially at the beginning of a run, it is acceptable to start counting injections after the last standard. However, samples and QCIs dispersed amongst the CCVSs must be counted as samples and/or injections. It is also important to note that an analytical run should consist of sequential injections. A run could potentially begin late one day and not end until sometime the next day. However, this does not mean that a run can last for more than a day simply because the maximum number of samples or injections has not been met. Run a new CCVS at the beginning of each daily run sequence, even if the previous sequence has not met the 10 sample, 14 injection limit.

7.7.3.   Criteria for CCVS

Retention time windows will be set according to the first CCVS of the day (or the mid-point standard in the curve if no CCVS is available) as in section 6.4. All subsequent CCVSs must meet the retention time window criteria in section 7.1.3.

CCVSs must also pass quantitative criteria. Quantitate all CCVSs using the initial calibration curve. Calculate the standard recovery. The CCVS recovery must be within $\pm 15\%$ of the true standard concentration.

7.7.4.   Corrective Action for CCVS

If a CCVS preceding a set of 10 samples fails quantitative criteria as described in section 7.7.3, it can be reanalyzed. If a successful CCVS cannot be analyzed a new initial calibration curve must be analyzed for the compounds that were out of control. Quantitative analysis is not allowed on a column that cannot pass the CCVS criteria in section 7.7.3, until a new initial calibration has been run on the column as in

section 6.7. CCVSs which follow a set of 10 samples are not required to meet criteria to validate the analysis of the preceding samples, but rather only samples which follow the CCVS.

7.7.5. Documentation for CCVS

The percent recovery of each compound should be summarized in a table or report. The CCVS should be filed in a manner that will ensure that it can be easily retrieved and referenced to all associated samples.

7.8. Preparation Blank

7.8.1. Definition & Use of Preparation Blank

The purpose of the preparation blank is to ensure that samples are not being contaminated by glassware, reagents, or the analytical system. To accomplish this it is necessary that the blank be carried through all stages of the sample preparation and measurement steps. See the appropriate extraction SOP for specific instructions on preparing the preparation blank.

7.8.2. Frequency of Preparation Blank

Preparation blanks will be provided by extraction personnel, with every extraction set. (See section 1.1 for the definition of extraction set.) Preparation blanks will also be provided with extraction sets done for quality control purposes such as method validation studies and MDL studies. The analyst should make every effort to run preparation blanks along with the corresponding extraction set.

7.8.3. Criteria for Preparation Blank

No target compounds may be detected above the reporting limits in Table 1.

7.8.4. Corrective Action for Preparation Blank

It is possible that non-target interferences on the primary column could cause a blank to appear contaminated with target compounds. Therefore, if a blank appears contaminated on the primary column and the secondary column has passed initial calibration or CCVS criteria, the blank may be reevaluated on the secondary column. If a blank is contaminated, the extraction batch is out of control. All associated samples and QCIs must be reextracted and reanalyzed.

7.8.5. Documentation for Preparation Blank

All hits above the reporting limits should be clearly indicated on the chromatogram or report. All preparation blanks should be filed in a manner that will ensure that they can be easily retrieved and referenced to all associated samples.

7.9. Matrix Spikes and Matrix Spike Duplicates (MS/MSDs)

7.9.1. Definition & Use of MS/MSD

The purpose of the MS/MSD is to confirm that the matrix being analyzed is not interfering with the recovery of the analytes. Matrix spikes are defined as spiked client samples. If this method is to be used for the analysis of the single component pesticides in Table 8, the MSs must contain all of the single component pesticides at the levels specified in Table 8. If this method is to be used only for the analysis of the multicomponent analytes in Table 8, use the most representative multicomponent analyte for MS spiking. See the appropriate extraction SOP for specific instructions on preparing an MS.

7.9.2. Frequency of MS/MSD

When sample volumes permit, MS/MSDs will be provided by extraction personnel with every "extraction batch". See section 1.1 for the definition of extraction batch. If extraction personnel routinely lack adequate sample volume for MS/MSD extraction, management should coordinate an effort to get clients to send more sample. The analyst should make every effort to run the MS/MSD along with the corresponding extraction batch.

7.9.3. Criteria for MS/MSD

The recovery of all target analytes must meet the percent recovery limits in Table 8.

7.9.3.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked sample}) - (\text{Unspiked sample})}{\text{Spike Value}} \times (100)$$

7.9.3.2. The calculation for Precision as Relative Percent Difference (RPD) is:

$$\text{RPD} = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{(\text{Sum of the Values}) / 2}$$

Precision (RPD) must be less than 20%.

7.9.4. Corrective Action for MS/MSD

It is possible that interferences on the primary column could cause a matrix spike to be out of control. Therefore, if a matrix spike does not meet acceptance criteria on the primary column and the secondary column has passed initial calibration and CCVS criteria, the matrix spike and the sample may be reevaluated using the secondary column. If

a matrix spike cannot meet acceptance criteria, the LCS must be evaluated for the analytes failing the criteria. If the LCS is acceptable but MS/MSD does not meet acceptance criteria, the sample data should be flagged appropriately.

7.9.5. Documentation for MS/MSD

The percent recovery of each compound should be summarized in a table or report. The MSs should be filed in a manner that will ensure that they can be easily retrieved and referenced to all associated samples.

7.10. Laboratory Control Sample (LCS)

7.10.1. Definition & Use of LCS

The purpose of the LCS is to establish that the techniques being used are not the cause of a matrix spike being out of control. If this method is to be used for the analysis of single component pesticides in Table 8, the LCS must contain all the single component pesticides, in Table 8, which are targets. If this method is not to be used for the analysis of the single component pesticides in Table 8, spike the LCS with the multicomponent analyte that was used for matrix spiking. The LCS may be used to validate method performance if the MS/MSD is out of control. See the appropriate extraction SOP for specific instructions on preparing the LCS.

7.10.2. Frequency of LCS

LCSs will be provided by extraction personnel with every "extraction set". The analyst should make every effort to analyze the LCSs along with the corresponding extraction batch; however the LCS only needs to be evaluated when the MS/MSD fails.

7.10.3. Criteria for LCS

When evaluated, LCSs must pass the percent recovery limits (p) in Table 8. Statistically determined control limits will be developed from LCS performance data and updated yearly (as in section 7.11.3). The LCS must also meet these limits.

7.10.4. Corrective Action for LCS

It is possible that interference from other target analytes could cause an analyte to fail LCS acceptance criteria on the primary column. Therefore, if an LCS fails acceptance criteria on the primary column and the secondary column has passed initial calibration or CCVS criteria, the LCS may be reevaluated using the secondary column. If the LCS cannot meet the limits outlined in section 7.10.3, it can be reanalyzed. If an MS/MSD or LCS cannot be analyzed successfully, the extraction batch is out of control. All associated samples and QCIs must be reextracted and reanalyzed.

7.10.5. Documentation for LCS

When an LCS has been evaluated, the percent recovery of each compound

should be summarized in a table or report. The LCS should be filed in a manner that will ensure that it can be easily retrieved and referenced to all associated samples.

7.11. Surrogates

7.11.1. Definition & Use of Surrogates

The purpose of surrogates is to verify that each sample was properly extracted, that the analytical system was working properly when the sample was run, and that there were no matrix interferences. A surrogate is simply a non-target compound that is chemically similar to the analytes. Surrogates are added to each sample and QCI prior to extraction. The surrogates used in this SOP are Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCMX). During the analysis of the samples and QCIs, the recovery of the surrogates is calculated and evaluated to determine if the extraction and analysis were performed properly. Quantitate surrogates using the primary column.

7.11.2. Frequency of Surrogates

Surrogate is added to every sample and QCI, prior to extraction, by extraction personnel.

7.11.3. Criteria for Surrogates

Although two surrogates are used, only one of them needs to pass recovery criteria. Surrogate recovery acceptance limits are determined for a matrix after 30 samples of the matrix have been analyzed. After the 30 samples have been analyzed, calculate the mean percent recovery (mean) and standard deviation of the percent recovery (s) for each surrogate. The control limits for that matrix are calculated according to the equations:

$$\text{Upper Control Limit (UCL)} = \text{mean} + 3s$$
$$\text{Lower Control Limit (LCL)} = \text{mean} - 3s$$

DCB is the primary surrogate and should be used whenever possible. If DCB exceeds the control limits outlined above, evaluate TCMX. Proceed with corrective action when both surrogates exceed control limits. Surrogate recovery limits for each matrix should be updated annually. The current advisory limts are 40 % to 160 %.

7.11.4. Corrective Action for Surrogates

If a surrogate fails acceptance criteria, check all calculations for error. It is possible that interferences on the primary column could cause surrogates to fail acceptance criteria. Therefore, if the analyst believes that interference on the primary column caused both surrogates to fail recovery criteria and the secondary column has passed initial calibration or CCVS criteria, the surrogate(s) may be re-evaluated using the data from the secondary column. If the surrogates fail acceptance criteria on both columns the extract should be re-analyzed. do not re-analyze an extract more than once, because

of surrogate problems, without first consulting your supervisor. If neither surrogate in the sample meets the acceptance criteria after re-analysis a problem is indicated and the sample should be re-extracted and re-analyzed. If re-extraction is not possible, the corresponding data must be flagged "surrogate recoveries were outside acceptance limits".

7.11.5. Documentation for Surrogates

The percent recoveries calculated for the surrogates should be documented on the chromatogram or report and entered into Labsys 2. Since the surrogate criteria may change from time to time, a file should be kept to document all past and present surrogate acceptance criteria and the dates that each criterion was in use. File the chromatograms according to their specific use.

8. REFERENCES

1. USEPA SW-846, Method 8080A, "Organochlorine Pesticides and PCBs", Revision 1, September 1994.

2. USEPA SW-846, Method 8000A, "Gas Chromatography", Revision 1, July 1992.